PROCESS FOR SEQUESTRATING CARBON IN THE FORM OF A MINERAL IN WHICH THE CARBON HAS OXIDATION NUMBER +3

The invention relates to a process for sequestrating carbon emitted into the atmosphere in the form of CO_2.

Prior art

The electrochemical reduction of CO_2 has been studied by a number of researchers, spanning the need to use it as a vast carbon supply source to attempts to use it as a source of energy in the form of methane.

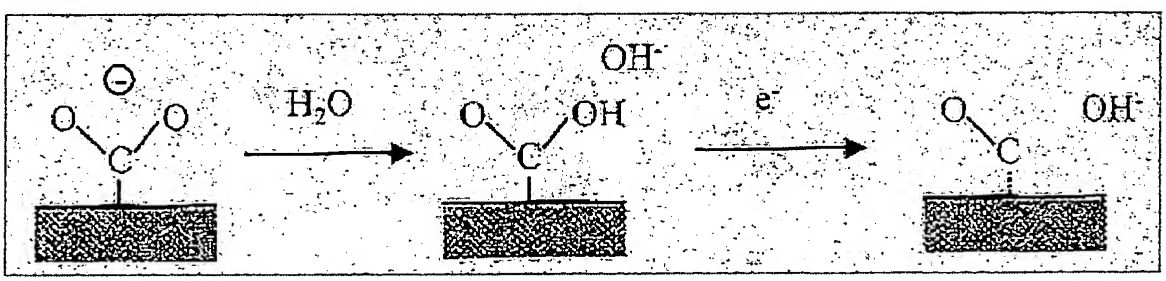
Studies on the electro-reduction of CO_2 began in the middle of the 1960s. They show that changes in the medium, whether it is aprotic or not, and the electrode, which determines the interactions of the intermediate carbonyl radical with the surface, lead to the formation of various constituents, including: carbon monoxide, formic acid, methane and ethane, alcohols such as methanol, ethanol and propanol, and oxalic or glycolic acid.

Thus, CO_2 electro-reduction reactions on copper electrodes in a potassium carbonate medium produce yields of the order of 30% of methane.

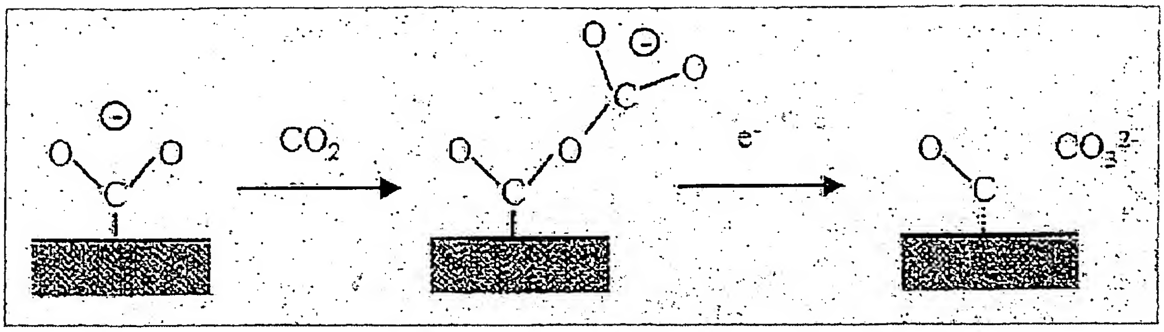
Studies are known which have identified products which are preferentially obtained for media of a more or less aqueous nature and for different natures of electrodes.

First case: The CO_2^- radical is adsorbed on the electrode

Aqueous medium (Au, Ag, Cu or Zn electrode): Carbon monoxide is formed

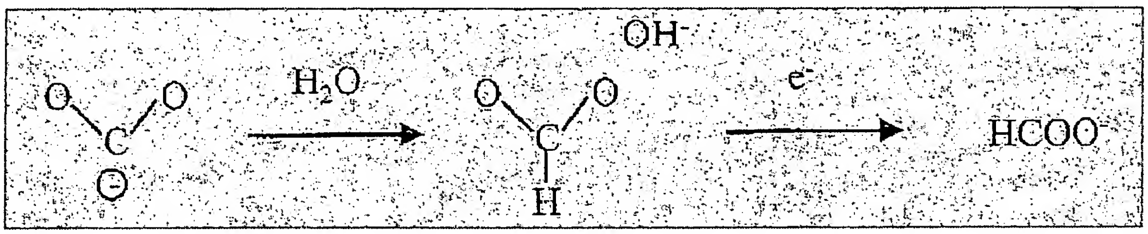


Non-aqueous medium (Au, Ag, Cu, Zn, Cd, Sn or In electrode): Carbonate is formed

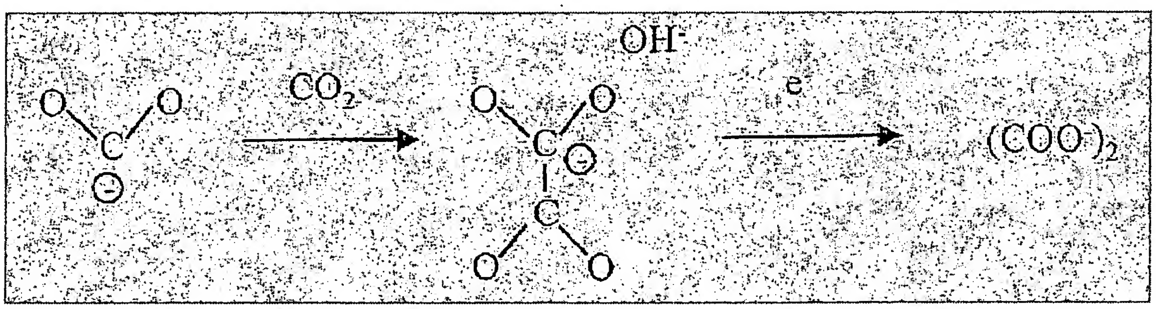


Second case: The CO_2^- radical is not adsorbed on the electrode

Aqueous medium (Cd, Sn, In, Pb, Tl or Hg electrode): Formic acid is formed



Non-aqueous medium (Pb, Tl or Hg electrode): Oxalic acid is formed



In this context, experiments have also been carried out on CO_2 in the gas phase on perovskites, which preferentially produce alcohols.

Studies concerning the capture of CO_2 by organic solvents have also been carried out – they finish by producing CO_2 in the liquid form. That CO_2 is then injected into the ocean bottom or, preferentially, into subterranean cavities. However, the durability of such storage facilities over very long periods is uncertain.

DESCRIPTION OF THE INVENTION

A novel process for sequestrating carbon emitted into the atmosphere in the form of CO_2 has now been discovered which can allow carbon to be sequestrated at moderate energy costs,

and more particularly limits the emission of greenhouse gases into the atmosphere consequent upon the combustion of fossil hydrocarbons.

The sequestration process of the invention comprises:

a) a step for concentrating CO_2 in the liquid phase;

b) a step for electro-reduction in an aprotic medium to a compound in which the carbon changes to oxidation number +3 in the form of oxalic acid or formic acid;

c) if appropriate, a step for re-extracting oxalic or formic acid in the aqueous phase; and

d) a step for mineralization by reaction with a compound of an element M, resulting in a stable compound in which the atomic ratio C/M is about 2/1.

The successive steps of the process of the invention are described in more detail below.

The liquid phase concentration step a) may be carried out using a plurality of methods.

A first method i) consists of liquefying CO_2 using conventional CO_2 capture processes. The liquid CO_2 is then obtained under pressure, for example in the supercritical state.

A further pathway ii) consists of absorbing the CO_2 in a polar aprotic liquid which is not miscible with water or miscible with water in various proportions. Acetonitrile may be cited as an example.

In accordance with a further pathway iii), we envisage absorption of CO_2 in an aprotic ionic liquid (or "molten salt") which is not miscible with water or miscible with water in various proportions. A particularly appropriate ionic liquid is 1-butyl-3-methylimidazolium hexafluorophosphate, represented by the formula $[BMIM]^+PF6^-$.

A still further pathway iv) consists of absorbing CO_2 in an aqueous phase containing an alcohol and/or an amine.

A further method v) consists of absorbing CO_2 in the hydrated form in a solvent, for example aqueous, activated by an enzymatic pathway. The enzyme which activates hydration is generally carbonic anhydrase. In this case, the solution obtained may then be recycled to an

aqueous phase absorption process in the presence of an alcohol and/or amine as defined in iii) above.

The aqueous solution obtained in the absorption method as defined in iv) or v) above may also be recycled to a liquefaction process as defined in i) above.

Further, the aqueous solutions obtained in processes as defined in iii) or iv) above are in general transferred into an ionic liquid medium which is insoluble in water by a liquid-liquid extraction process.

Depending on the method employed to carry out the first step of liquid phase concentration of the process of the invention, the liquid phase obtained will consist of liquid CO_2 or a solution of CO_2 or carbonic acid in a polar aprotic liquid which is not miscible with water or miscible with water in varying proportions, or in a non-aqueous ionic liquid (molten salt) with a variable miscibility with water.

The second step of the process of the invention consists of electro-reduction of CO_2 or concentrated carbonic acid in the liquid phase (oxidation number +4) to a compound in which the carbon has an oxidation number of +3. It is carried out in the liquid phase obtained in the preceding step, in general at a pH in the range 3 to 10, preferably in the range 3 to 7 and with an anode maintained at a potential of +0.5 to -3.5 volts with respect to a standard hydrogen electrode. The anode may be constituted by platinum, for example diamond doped with boron or carbon doped with nitrogen.

By means of this electro-reduction, the oxalic ion (in the form of oxalic acid or the oxalate) or the formic ion (in the form of formic acid or the formate) is formed.

If appropriate, electro-reduction step b) is carried out in liquid CO_2 under pressure.

Electro-reduction step b) may also be carried out in subterranean CO_2 storage into which liquid CO_2 may have been injected, if appropriate.

The third step c) of the process of the invention consists of a re-extracting the oxalic acid (or oxalate) or formic acid (or formate) using an aqueous phase. It is carried out when the

electro-reduction has been carried out in a non-aqueous phase. The formation of formic acid by electro-reduction is generally carried out in the aqueous phase. It is not necessary in this case to carry out this step c) for re-extraction by an aqueous phase.

The final step d) of the process of the invention (mineralization step) generally consists of attack with a carbonated mineral, for example calciferous or magnesia-containing, with an aqueous solution of oxalic acid (or oxalate) or formic acid (or formate) from the electro-reduction step (optionally after re-extraction). Said solution is reacted with a compound of an element M to produce a mineral in which the atomic ratio C/M is about 2/1.

The reaction of the oxalic or formic compound with the carbonated mineral produces one mole of CO_2 per C_2O_4,

$$MCO_3 + (COOH)_2 \rightarrow MC_2O_4 + CO_2 + H_2O \text{ or}$$

$$MCO_3 + 2HCOOH \rightarrow M(HCO_2)_2 + CO_2 + H_2O$$

The CO_2 liberated, half that used at the start, may be reintroduced into the inventive process cycle at the first step.

The element M may be any metallic element with an oxidation number of +2. It is usually calciferous or magnesia-containing. The compound of element M may then, for example, be a calciferous or magnesia-containing rock. The preferred element M is calcium. The mineral formed is preferably a calcium oxalate such as Whewellite, $CaC_2O_4.H_2O$.

The process of the invention (or only the last step) may be carried out ex situ or in situ in the calciferous or magnesia-containing rock.

Next, the final mineralization step d) may take place by bringing the solution of oxalic or formic acid into contact with a sedimentary rock for example calciferous or magnesia-containing, preferably by injection into the substratum.

It will be noted that as regards the energy balance of the process of the invention, the energy invested to change from carbon +4 to carbon +3 in the electro-reduction reaction of the

second step is not lost: it is in fact stored in the mineral oxalate or formate which is formed. Clearly, the oxalic or formic acid could be re-extracted subsequently for use in combustion, for example in situ. It may concern oxidation, for example bacterial, in situ or ex situ. In these processes, the carbon would move to an oxidation number of +4.

EXAMPLES

Example 1

Liquid CO_2 was obtained by a conventional liquefaction process.

The reactor was filled with CO_2 liquid under pressure (50 bars at ambient temperature) and steadily supplemented with water to maintain the CO_2/H_2O molar ratio to about 100 to orientate the reaction towards the synthesis of oxalic acid. Tetra-ammonium perchlorate was added in an amount of 0.1 mol/l.

The electrode was platinum and the current density was 5 mA/cm^2. The electrode potential was -3 V with respect to the potential of the Fe/Fe^+ couple. The solution was stirred to limit concentration effects at the electrodes.

The quantity of CO_2 to be electro-reduced fixed the quantity of electricity required.

After electro-reduction, the oxalic acid formed was injected into a receptacle containing calcium carbonate. The oxalic acid reacted with the carbonate to form a calcium oxalate. The increase in mass of the dried and cleaned residue demonstrated the sequestration of CO_2 in the mineral form.

Example 2

Liquid CO_2 was obtained by a conventional liquefaction process.

It was supplemented with tetra-ammonium perchlorate and injected into a subterranean cavity containing calciferous or magnesia-containing rocks. Electro-reduction was carried out directly in the cavity using a platinum electrode. The current density was 5 mA/cm^2. The electrode potential was -3 V with respect to the potential of the Fe/Fe^+ couple. The solution was stirred to limit concentration effects at the electrodes.

The synthesized oxalic acid reacted with the calciferous or magnesia-containing rocks liberating CO_2, which was also reduced, and a divalent cation which precipitated with the oxalate. The reactions finally resulted in the sequestration of CO_2 by a mineral pathway. The CO_2 liberated was recycled to the liquefaction step.

Example 3

CO_2 was absorbed with water in the presence of carbonic anhydrase as described in US-A-6 524 843.

Tetra-ammonium perchlorate was added in an amount of 0.1 mol/l.

The electrode was platinum and the current density was 5 mA/cm^2. The electrode potential was -3 V with respect to the potential of the Fe/Fe$^+$ couple. The solution was stirred to limit concentration effects at the electrodes.

The quantity of CO_2 to be electro-reduced fixed the quantity of electricity required.

After electro-reduction, the formic acid formed was injected into a receptacle containing calcium carbonate. The formic acid reacted with the carbonate to form a calcium formate. The increase in mass of the dried and cleaned residue demonstrated the sequestration of CO_2 in the mineral form.

Example 4

CO_2 was absorbed into an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, represented by the formula [BMIM]$^+$PF6$^-$.

Tetra-ammonium perchlorate was added in an amount of 0.1 mol/l.

The electrode was platinum and the current density was 5 mA/cm^2. The electrode potential was -3 V with respect to the potential of the Fe/Fe$^+$ couple. The solution was stirred to limit concentration effects at the electrodes.

The quantity of CO_2 to be electro-reduced fixed the quantity of electricity required.

The CO_2-saturated ionic liquid was brought into continuous contact with an aqueous solution which extracted the oxalate therefrom.

The aqueous oxalic acid solution which was formed was injected into a receptacle containing calcium carbonate. The oxalic acid reacted with the carbonate to form a calcium oxalate. The increase in mass of the dried and cleaned residue demonstrated the sequestration of CO_2 in the mineral form.